

METASTABLE ISOMERS: A NEW CLASS OF INTERSTELLAR MOLECULES

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ABSTRACT

The abundances of a variety of metastable isomers of small organic molecules, analogous to HNC/HCN, in dense interstellar clouds are considered. These metastable species, some of which are thought to exist as intermediates in laboratory organic chemical reactions, are of considerable interest to chemists. Current ideas of gas-phase, ion-molecule chemistry are utilized here to demonstrate that such metastable species should often be present in dense clouds in sufficient abundance to be observed. Unfortunately, the spectral constants of metastable isomers have rarely been determined in the laboratory, and quantum chemical calculations of a varying degree of accuracy must be utilized; we include here the results of some new quantum chemical calculations. The interstellar chemistry and expected microwave spectra of a representative sample of possibly important interstellar metastable isomers are discussed.

Subject headings: interstellar: matter — interstellar: molecules — molecular processes

I. INTRODUCTION

In the last decade, radioastronomical observations of microwave emission spectra have led to the discovery of an extensive and intricate gas-phase interstellar chemistry (for a review, see, e.g., Watson 1976). At present, some 4 dozen different molecular species, ranging in size from two to eleven atoms, have been identified. The first compounds to be observed were generally familiar stable species such as water, ammonia, and carbon monoxide; a number of simple organic alcohols, aldehydes, amines, and substituted acetylenes have also been found. Although these are all familiar compounds, their existence in interstellar space was quite astonishing at first because of the assumed harshness of the interstellar environment.

Interstellar chemistry is still imperfectly understood, although much progress has been made (for a recent survey, see, e.g., Herbst 1978a). Most of the observed molecular species appear to be located in dense interstellar clouds that are light years in extent, possess gaseous densities in the range 10^3 – 10^6 molecules per cm^3 , and have temperatures below 100 K. Dust grains associated with the gas scatter and absorb stellar radiation so that molecules in dense clouds are protected from photodissociation. Elemental abundances in dense clouds are presumed to follow the well-known cosmic abundance ratios (Allen 1973): H(1.0), He(0.09), O(7×10^{-4}), C(3×10^{-4}), and N(9×10^{-5}). There is convincing evidence that hydrogen is overwhelmingly in its molecular form. It is generally assumed that hydrogen atoms are converted to H_2

molecules on the surface of the dust grains (Hollenbach, Werner, and Salpeter 1971) because no competitive gas-phase mechanism has been found. Whether other molecules are formed on the grains is still conjectural; a major theoretical problem is removing molecules from cold grains once they have been formed. Once considerable H_2 is synthesized, it can be shown that there is sufficient ionization caused by cosmic rays impinging on dense clouds to drive a rapid and complicated gas-phase ion-molecule chemistry which can explain, at least semiquantitatively, the concentration of many of the observed species (Herbst and Klemperer 1973; Mitchell, Ginsburg, and Kuntz 1978). All detailed ion-molecule models of dense clouds show the chemistry to be dominated by kinetic rather than thermodynamic constraints.

In addition to common stable compounds, ion-molecule chemistry schemes predict that some molecular ions and free radicals will be rather abundant. A selection effect was probably responsible for the initial discovery of only simple stable species, since only molecules with spectral frequencies measured in the laboratory could be easily searched for in interstellar sources. That this was the case became obvious in the early 1970s when several rather strong interstellar signals were observed at frequencies which did not correspond to any known laboratory species. The first of these, dubbed X-ogen, at 89.189 GHz (Buhl and Snyder 1970), was tentatively identified as the $J = 1-0$ transition of the molecular ion HCO^+ (Klemperer 1970) based on a simple estimate of its rotational frequency. The second, dubbed Y-ogen or X_2 , at 90.665 GHz, was tentatively identified as the $J = 1-0$ transition of HNC, the metastable isomer of the

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known interstellar species HCN (Snyder and Buhl 1971). Subsequently, a multiplet around 87.3–87.4 GHz was identified as the $J = 1-0$ transition of the CCH radical (Tucker, Kutner, and Thaddeus 1974) partly on the basis of a theoretical estimate of its rotation constant and partly on the basis of some previous matrix isolation studies of its hyperfine constants. A triplet of lines near 93.2 GHz was assigned to the $J = 1-0$ transition of the molecular ion N_2H^+ on the basis of theoretical calculations of its rotation constant and nitrogen quadrupole splitting (Turner 1974; Green, Montgomery, and Thaddeus 1974; Thaddeus and Turner 1975). Recently, two doublets with a common rotation constant have been identified as the $J = 9-8$ and $10-9$ transitions of the C_3N radical (Guélin and Thaddeus 1977), and another set of four doublets has been attributed to the C_4H radical (Guélin, Green, and Thaddeus 1978). Spurred on by these astrophysical observations, renewed laboratory efforts have now confirmed the identifications of HCO^+ , N_2H^+ , and HNC (Woods *et al.* 1975; Saykally *et al.* 1976a; Saykally *et al.* 1976b). The free radicals, on the other hand, have still not yielded to terrestrial experiments. Isotopic variants of some of these species have now also been observed in the laboratory, in space, or both.

These observations are particularly interesting because the observed species have only transient existences in the laboratory, where they are quite reactive. However, under the extreme interstellar conditions of low density and low temperature, these unusual species can have appreciable lifetimes and abundances. It is reasonable to assume that many other free radicals and molecular ions exist in appreciable abundance under interstellar conditions and that, consequently, dense interstellar clouds provide a convenient "laboratory" for the observation of transient molecular species which, although of great chemical interest, have generally defied attempts to observe their spectra in terrestrial experiments.

In the present paper, we point out the fact that, according to current ideas of interstellar ion-molecule chemistry, many metastable isomers of stable molecules analogous to the case of HNC and HCN probably have observable abundances in dense interstellar clouds. Detection (or nondetection) of these species would clarify our understanding of important interstellar synthetic pathways. In addition, many of these compounds are believed to be intermediates in important organic reactions, although they have rarely been isolated or directly observed in the laboratory. Observation of the microwave spectra of these species in interstellar clouds would provide valuable information about their structures which in turn would improve our understanding of the roles they play in terrestrial chemical reactions.

The difficulties inherent in this program should be apparent. A major obstacle is our lack of knowledge of the spectral constants of these metastables. In most cases, not even the energetics are well known. Thus, unless there is a substantial energy barrier to rearrangement, an isomer will have no true existence as

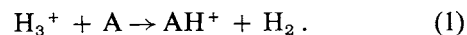
a metastable species. The height of such barriers, as well as the energy of the metastable relative to the ground state, is not well known. Although some information has been inferred by considering the kinetics of organic reactions in which a species is a postulated intermediate, our best and most direct information about these species comes from quantum theoretical calculations. A problem, however, is that quantum calculations, in order to be made tractable, require fairly severe approximations for all but the simplest systems, and the accuracy of these is best gauged by comparing with experimental data for related systems. It is not uncommon for different calculations, each using rather sophisticated approximations, to differ significantly on energy and spectral constants for these metastable species.

Despite these difficulties, the situation is not impossibly bleak. As noted, HCO^+ , HNC, N_2H^+ , C_2H , C_3N , and C_4H were all identified in interstellar observations without the benefit of laboratory spectral data. Quantum theoretical calculations played important roles in these identifications, and, in the case of C_4H , a theoretical prediction provided the basis for a successful astrophysical search. However, ideas of interstellar chemistry also played important roles in these identifications. Also of extreme utility were "fingerprints" due to fine and hyperfine structure in the spectra of these species. We believe that this same combination of quantum theory, models of interstellar chemistry, and spectral fingerprints will make it possible to identify a number of metastable species in interstellar space. The potential information about interstellar chemistry as well as about the structure of organic metastables will make such identifications well worth the effort.

In the rest of this paper, we will consider some of the more likely and/or more interesting of the potentially observable species. The next section will review current ideas of interstellar chemistry as they relate to the production of metastables. In § III, we will discuss specific metastable species, including likely chemical synthetic paths and estimates of interstellar abundances and spectral constants. The results of some new quantum chemical calculations will be presented.

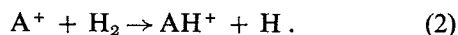
II. INTERSTELLAR CHEMISTRY

Detailed models of gas-phase interstellar chemistry in dense clouds are complex (Herbst and Klemperer 1973; Iglesias 1977; Mitchell, Ginsburg, and Kuntz 1978); we discuss here only some salient features concerning the abundances of certain metastable isomers of stable molecules. Because dense interstellar clouds are composed primarily of H_2 molecules, the dominant product of cosmic-ray ionization, H_2^+ , reacts rapidly to produce H_3^+ , which, in turn, can transfer a proton exothermically to many neutral species:

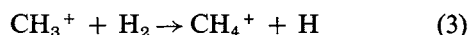


Exothermic ion-molecule reactions of this class usually have negligible activation-energy barriers (Huntress

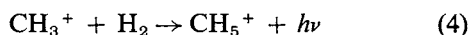
1977) and proceed rapidly at interstellar temperatures. Ions formed in this manner, by more involved chemical pathways or by photoionization, can add hydrogens via hydrogen atom abstraction reactions:



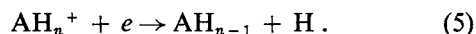
These reactions are often fast, as long as they are exothermic (Huntress 1977), and successive hydrogens can be added rapidly to the molecular ion. Where hydrogen abstraction (eq. [2]), is slow, hydrogenation can, in some cases, proceed further via radiative association (Herbst 1976). For example,



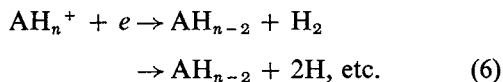
is endothermic and does not occur at interstellar temperatures, whereas



is probably an important process (Smith and Adams 1978; Herbst 1976). Ions which do not react rapidly with molecular hydrogen are depleted via reactions with other neutrals and via dissociative recombination with electrons:



(If A stands for a species with more than one atom, then clearly there are additional exit channels in which only one chemical bond is broken.) These latter reactions are very rapid at low temperatures and are so exothermic (by typically 100–150 kcal per mol) that there is almost always enough energy to cause further dissociation (Herbst 1978*b*); for example,



The branching ratios among the various energetically possible channels have not been measured for any dissociative recombination reaction. This is unfortunate because these ratios are often crucial for predicting relative abundances of neutral interstellar species.

We propose here a simple new model for branching ratios in dissociative recombination reactions which is based on generally applicable ideas of molecular electronic structure and which also appears to be consistent with earlier quantitative theoretical ideas (Bardsley and Biondi 1971; Herbst 1978*b*). In order for an ion to capture an electron, energy must be given up; otherwise, the system, which is in an autoionizing state, will reemit the electron in a time which is typically on the order of 10^{-14} s. For a molecular ion, it is generally possible to stabilize the system on a sufficiently rapid time scale by converting potential energy into kinetic energy of the nuclei, i.e., vibrational motion. While the system is now stable with respect to autoionization, it is still unstable with respect to dissociation. As noted above, there is generally enough excess energy to cause extensive fragmentation and rearrangement of the molecular structure. The rates at

which different products are formed then depend on the rate at which the available energy can be channeled into nuclear motion along the various exit channels, and this depends ultimately on the shape of the potential energy surface near the equilibrium geometry of the parent ion. Although detailed calculations have not yet been done for any polyatomic case, the following considerations should hold in general. The rate at which potential energy is converted to kinetic energy is inversely proportional to product mass, so that hydrogen atoms are likely to be expelled more rapidly than heavy atoms or molecular fragments. Further, if there are several hydrogen atoms, we expect that any one will be expelled with approximately equal probability, especially if this departure leads, with only minor additional adjustments of nuclear positions, to a (meta-)stable structure, since then an energy barrier in the exit channel is unlikely. On the other hand, products which require extensive nuclear rearrangement seem unlikely since this entails breaking chemical bonds and forming others, which generally implies energy barriers in the exit channel. In summary, this model predicts that dissociative recombinations of protonated species will result in loss of any one of the hydrogen atoms with approximately equal probability, but no extensive nuclear rearrangements. Of course, it must be remembered that exceptions to this generalization may occur owing to peculiarities of the potential energy surface for a specific system.

A key point in the present discussion is that the dissociative recombination step provides a mechanism for producing isomeric neutral species which are not in thermal equilibrium. Consider the case of HCN and HNC. Hydrogen isocyanide is calculated to lie 15 kcal per mol above hydrogen cyanide (Pearson, Schaefer, and Wahlgren 1975) and would have negligible abundance if the two species were in thermal equilibrium at interstellar temperatures of less than 100 K. However, HNC and HCN are found to have roughly equal abundances in dense interstellar clouds! A most reasonable explanation (Watson 1974, 1976) is that both of these species have a common precursor, the linear ion $HCNH^+$ (Pearson and Schaefer 1974):



(The $HCNH^+$ ion is formed from both CN and NH_3 via ion-molecule pathways; see Herbst and Klemperer 1973; Mitchell, Ginsburg, and Kuntz 1978.) A branching ratio near unity in this reaction is required to explain the astrophysical observations; this has been justified via a model (phase space) calculation (Herbst 1978*b*) and is also in accord with the model presented above. Of course, further theoretical work or, preferably, experimental measurements to determine this and other important branching ratios in dissociative recombination reactions, would be most useful. Nonetheless, the above mechanism for HCN and HNC formation, coupled with equal depletion rates for these two species, offers a plausible explanation for their observed interstellar abundances.

While the reaction scheme outlined above has been considered as a formation mechanism for HNC and HCN, it does not seem to be appreciated that analogous reaction sequences can lead to significant abundances of other metastable isomers of well-known stable molecules. It will prove convenient to distinguish between two somewhat different reactive pathways for synthesizing a species, A, and its metastable isomer, A*. In the first, or primary method, A is formed via dissociative recombination of the precursor ion, AH_n^+ , which in turn has been formed by a sequence of gas-phase (ion-molecule) reactions. If dissociative recombination of the precursor can lead to formation of both A and A* (cf. the case of $HCNH^+$ as precursor to HCN and HNC, eqs. [7]), then, depending on branching ratios, these may easily have comparable abundances. In fact, the relative abundances of A and A* will strongly reflect the branching ratio in the dissociative recombination step. (We assume here that A and A* are also destroyed at comparable rates, which seems to be reasonable; see the discussion in the Appendix.) Although ion-molecule models suggest that such primary syntheses may be common, some interstellar species are undoubtedly not formed in this manner; that is, their synthesis does not involve dissociative recombination of a protonated precursor. For example, a species might be synthesized primarily via a sequence of neutral reactions or on the surface of grains. Nonetheless, a metastable species A* may still be formed in appreciable abundance starting with protonation of the stable species A (details of whose synthesis need not be known). We will call this a secondary synthesis. In the Appendix, we show that if certain assumptions are made, then the ratio of a metastable isomer, A*, to the stable form, A, attainable under steady-state conditions via a secondary synthesis alone, is bounded by

$$g^*f \leq [A^*]/[A] \leq 1, \quad (8)$$

where g^* is the fraction of dissociative electron recombinations leading to A* and f is the fraction of the interstellar ion abundance which is able to protonate A. Whether $[A^*]/[A]$ lies near the upper or lower limit depends on the composition of the interstellar ion abundance. Estimates of f (normally the ratio of the sum of the HCO^+ , H_3^+ , and N_2H^+ concentrations to the total ion concentration) are 0.01 or greater (Herbst and Klemperer 1973; Mitchell, Ginsburg, and Kuntz 1978). Thus, if g^* is approximately one-half (as has been assumed, e.g., in the case of HNC/HCN), then a secondary synthesis can produce a significant abundance of the metastable isomer. Note that this requires only the (observed) existence of the stable species and a source of protons which is supplied by the cosmic-ray ionization. While secondary synthesis is expected to occur rather generally, it may lead to a ratio of $[A^*]$ to $[A]$ of only a few percent. On the other hand, for systems where primary synthesis can occur, this ratio may quite generally be near unity. The examples in the next section should help clarify these distinctions.

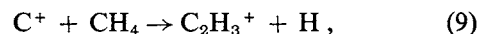
III. METASTABLE ISOMERS

In this section, we will consider the chemistry and spectral properties of a number of metastable isomers which are candidates for interstellar observations. The species discussed here constitute a representative, rather than an exhaustive list. It should become apparent from this discussion that the existence of metastable isomers is likely to be a rather general phenomenon, and that it is quite probable that many of these have observable abundances in dense interstellar clouds. It must be emphasized at the outset that many uncertainties exist in both the models of interstellar chemistry employed here and also in the theoretical values for molecular energy and structural parameters. An effort has been made to use the best available information and to indicate where the uncertainties are particularly severe. New quantum chemical calculations have been performed and are presented here for two of the metastable species.

a) Acetylene (HCCH)

Because carbon is one of the most abundant of the "trace" elements in interstellar space and because hydrogen is the dominant species, it is reasonable to assume that small hydrocarbons are relatively plentiful. A knowledge of the abundance of these species would be most helpful for an understanding of interstellar chemistry. Unfortunately, the simplest of these—methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), and ethane (C_2H_6)—all lack permanent dipole moments because of their high symmetry. Hence, they do not have pure rotational dipole spectra and are invisible in the microwave region. (Recently, acetylene has been detected via infrared observations in a circumstellar source; see Ridgeway *et al.* 1976; Hall 1978).

One of the routes by which interstellar acetylene is likely to be produced is via the vinyl ($C_2H_3^+$) ion, for example (Huntress 1977),



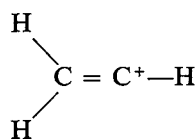
followed by dissociative recombination



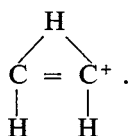
Using computed abundances of Mitchell, Ginsburg, and Kuntz (1978), and assuming ion-controlled destruction of HCCH, we estimate that these reactions produce an acetylene abundance approximately one-tenth that of methane (CH_4). The CH_4 abundance is not easily calculated because it depends critically on the rate of the poorly understood radiative association reaction $CH_3^+ + H_2$ (eq. [4]). However, Mitchell, Ginsburg, and Kuntz (1978) compute CH_4 fractional abundances of $\sim 10^{-9}$ using a conservative value for the rate of this radiative association. Use of a new value indirectly determined by Smith and Adams (1978) would boost the CH_4 abundance considerably.

Although no data exist on the structure of the vinyl

($C_2H_3^+$) ion, theoretical studies have indicated that it can have either a classical structure



or a nonclassical, bridged structure



A recent, accurate configuration interaction study (Weber, Yoshimine, and McLean 1976) indicates that the latter is slightly more stable, but that there is little barrier to rearrangement so that this ion may undergo large amplitude vibrational motions. The dissociative recombination step (eq. [10]) might also produce the metastable isomer of acetylene, vinylidene



There is no information, either experimental or theoretical, on the relative rates of (10) and (11), but both the model presented above and the phase space model calculation of Herbst (1978*b*) predict the rate of (11) to be comparable to that of (10). Thus, vinylidene may be formed in interstellar space via a primary synthesis, and hence have an abundance comparable with acetylene. Even if interstellar acetylene is produced in a manner which does not involve the vinyl ion as a precursor, vinylidene can still be formed efficiently via a secondary synthesis since acetylene is readily protonated via



where AH^+ can be H_3^+ , HCO^+ , or N_2H^+ .

A number of theoretical studies have been done on vinylidene (Hopkinson, Yates, and Csizmadia 1971; Dykstra and Schaeffer 1978; Davis, Goddard, and Harding 1977). From these it appears that the metastable species has a planar, Y-shaped, singlet electronic structure, lying about 40 kcal per mol above acetylene; however, the barrier against rearrangement to the stable structure appears to be rather low, probably in the range 6–8 kcal per mol. Because of the low barrier, there is some question as to whether vinylidene is, in fact, metastable, or whether zero-point vibrational motion might be sufficient to overcome (or tunnel through) the barrier. We tentatively assume that vinylidene has a fairly long lifetime against unimolecular rearrangement based on the fact that this requires a rather large, concerted motion of the hydrogens, as well as a simultaneous contraction of the C–C bond. Note also that typical interstellar thermal energies (100 K = 0.2 kcal per mol) are only a few percent of even this low barrier height.

TABLE 1
VINYLIDENE (H_2CC)

Parameter	Value and Accuracy	Reference
Rotation constants (GHz):		
<i>A</i>	302.0 (3%)	This work
<i>B</i>	38.7 (1%)	
<i>C</i>	34.3 (1%)	
Dipole moment (<i>D</i>).....	2.2 (10%)	Davis <i>et al.</i> 1977
Excitation energy* (kcal per mol).....	40 (10%)	Dykstra and Schaefer 1978

* Energy above lowest energy isomer (HCCH).

The rotational spectrum of vinylidene—a near prolate symmetric top—is entirely analogous to that of formaldehyde (H_2CO) which is structurally similar and which has similar spectral constants (see, e.g., Townes and Schawlow 1955). The most recent and most extensive calculations for vinylidene (Dykstra and Schaefer 1978) predict rotation constants which differ by more than 5% from the earlier calculations of Hopkinson, Yates, and Csizmadia (1971). Unfortunately, the level of approximation used by Dykstra and Schaefer (1978) is known to be rather inaccurate for geometrical parameters, although it should be reliable for energy quantities; the rotation constant for acetylene obtained in this calculation, for example, is in error by about 3%. We have performed new calculations, using a level of approximation which is usually reliable to better than 1% for rotation constants (see, e.g., Wilson and Green 1977); using this method, we find a rotation constant for acetylene of 35.5 GHz which may be compared with the experimental value of 35.3 GHz. Our rotation constants for vinylidene are given in Table 1, which summarizes information on this species.

b) Ethylene (H_2CCH_2)

Ethylene has no microwave spectrum and its interstellar abundance is entirely uncertain. For reasons which are not clear, carbon–carbon double bonds, as in ethylene, seem to be quite rare among interstellar molecules, although both single and triple bonds are common. Ethylene can presumably be formed in space through the ethyl carbonium ion (Huntress 1977):



followed by dissociative recombination:



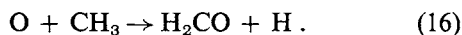
Using computed abundances of Mitchell, Ginsburg, and Kuntz (1978), we estimate this synthetic route to produce an ethylene abundance $\sim 10^{-3}$ that of methane. There is sufficient energy in the recombination step to produce as well the asymmetric metastable isomer, methyl carbene:



It appears that little theoretical work has been done on methyl carbene (Altmann, Csizmadia, and Yates 1974; Staemmler 1974). These studies predict that methyl carbene lies approximately 70 kcal per mol above ethylene, but that it is metastable with substantial barriers to rearrangement. Singlet and triplet electronic states are predicted by Hartree-Fock calculations to have about the same energy, which suggests that the ground state is a singlet if the usual corrections for correlation effects are applied. The geometry and hence the spectral constants have not been accurately determined. Because carbenes are thought to be intermediates in important organic reactions (see, e.g., Kirmse 1971), it would seem most desirable to obtain better theoretical information about this species.

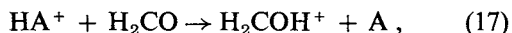
c) Formaldehyde (H_2CO)

Formaldehyde is a ubiquitous interstellar molecule. Producing adequate formaldehyde to match observations provided a severe test of early models of interstellar chemistry. The dominant synthetic route is now thought to be (Mitchell, Ginsburg, and Kuntz 1978; Dalgarno, Oppenheimer, and Black 1973) via the neutral reaction



Hydroxycarbene, HCOH , a well-known organic intermediate, has been predicted (Altmann *et al.* 1977; Lucchese and Schaefer 1978) to lie about 50 kcal per mol above formaldehyde and to possess a considerable barrier against rearrangement. Configuration interaction calculations (Lucchese and Schaefer 1978) indicate that HCOH has a ground-state singlet electronic structure; however, the reported spectral parameters are of insufficient accuracy for purposes of interstellar identification.

It seems unlikely that hydroxycarbene can be formed competitively at low temperatures via reaction (16) since this requires breaking two chemical bonds which would have a high activation barrier. However, it is energetically feasible to form it via a secondary synthesis because formaldehyde, once formed, can be protonated by H_3^+ and other interstellar species.



and dissociative recombination of the protonated form is expected to produce hydroxycarbene as well as formaldehyde. In any case, determination of the relative abundances of hydroxycarbene and formaldehyde would greatly aid our understanding of the interstellar chemistry of the latter.

d) Methanimine (H_2CNH)

Methanimine has been observed recently in the laboratory and subsequently in the interstellar medium (Godfrey *et al.* 1973). The interstellar synthesis of this species is unclear; one possibility is the reaction (Huntress 1977)



followed by dissociative recombination



This synthetic route has been studied semiquantitatively by Smith and Adams (1978). Our estimates indicate that this synthesis can produce a methanimine fractional abundance of $\sim 10^{-11}$, somewhat lower than observed values (Watson 1976). A metastable isomer of methanimine, which is of considerable chemical interest (see, e.g., Lwowsky 1970) is methyl nitrene, H_3CN . It is not clear whether methyl nitrene could be readily formed in the dissociative recombination step (eq. [19]). If the protonated species exists in the ethylenic structure as written, which seems likely (Kollman *et al.* 1973), then significant rearrangement would be required. The same problem would exist if methyl nitrene were formed via secondary synthesis, since protonation of methanimine would also produce the ethylenic structure. Clearly, more information about the possibility of rearrangements in protonation and in dissociative recombination reactions is needed to assess the likelihood of producing this species in space.

Rather extensive theoretical calculations on methyl nitrene have been done by Yarkony, Schaefer, and Rothenberg (1974), from which it appears that this metastable species lies only about 10 kcal per mol above methanimine and that it has a triplet electronic ground state. The rotational spectrum of methyl nitrene will be that of a symmetric top. The calculated rotation constants are included in Table 2. The rotational spectrum of methyl nitrene will have a great deal of hyperfine structure due to the triplet electronic state, the spins of the hydrogen nuclei, and the spin and quadrupole moment of the nitrogen nucleus. This structure should provide a distinctive fingerprint which could aid in identifying this species. Since many of the coupling constants are currently unknown, we have not made any detailed prediction of the hyperfine pattern at this time.

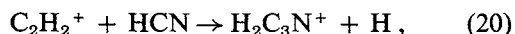
e) Cyanoacetylene (HCCCN)

Cyanoacetylene is a relatively abundant and widespread interstellar molecule. There is evidence that linear conjugated chains, of which HC_3N is proto-

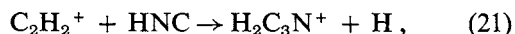
TABLE 2
METHYL NITRENE (H_3CN)

Parameter	Value and Accuracy	Reference
Rotation constants (GHz):		
A	159.0 (1%)	Yarkony <i>et al.</i> 1974
$B = C$	26.3 (1%)	Yarkony <i>et al.</i> 1974
Dipole moment (D).....	2.1 (10%)	Yarkony <i>et al.</i> 1974
Excitation energy (kcal per mol).....	10 (15%)	Yarkony <i>et al.</i> 1974

typical, may be particularly abundant in the interstellar environment. Thus the higher cyanopolyacetylenes, HC_5N , HC_7N , and HC_9N , have now also been detected in space. The reason for enhanced abundance of these long linear chains is not known, but an understanding of the interstellar chemistry of cyanoacetylene might offer some clues. One possible ion-molecule synthesis of HC_3N is (Huntress 1977)



and/or

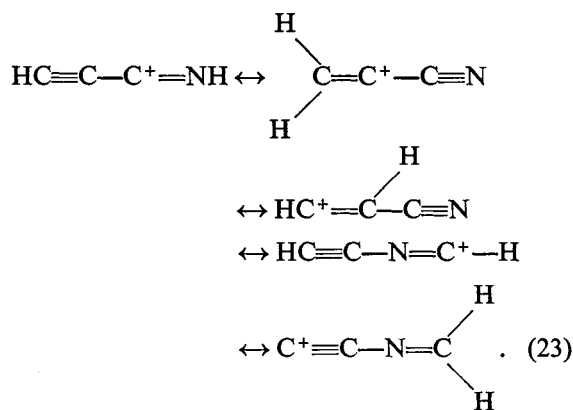


followed by dissociative recombination



Based on the calculated C_2H_2^+ fractional abundance of Mitchell, Ginsburg, and Kuntz (1978) we estimate that this synthetic route will fail by at least two orders of magnitude to produce enough HC_3N to match observations. A boost in the calculated CH_4 abundance (see the discussion in § IIIa) would help somewhat by raising the expected C_2H_2^+ abundances. The possibility of alternate synthetic routes must be considered. Even if HC_3N and metastable isomers are not produced via a primary synthesis such as equations (20)–(22), metastable species can still be produced in a secondary synthesis, and these should be observable with current sensitivity even if their abundances are only a few percent that of HC_3N .

There seems to be little information about the structure of $\text{H}_2\text{C}_3\text{N}^+$, although several (meta-)stable forms, including both CCCN and CCNC skeletons, seem possible since they have standard valence bond structures, e.g.,



Depending on the structure(s) of $\text{H}_2\text{C}_3\text{N}^+$ and branching ratios in the dissociative recombination step, (eq. [22]), observable abundances of various metastable isomers might be formed. One of these, isocyanoacetylene (HC_2NC), has been suggested by Wilson (1978) as a likely interstellar species by analogy with HCN and HNC . Wilson has performed Hartree-Fock calculations which indicate that HC_2NC lies less than 20 kcal per mol above HC_3N and that the

rotation constant of this species (assumed to be linear) is 5.08 GHz with an estimated uncertainty of about 1%. However, based on simple binding arguments and on analogy with known species, we expect that the most stable form of the protonated ion is HC_3NH^+ . Our model then predicts that the metastable C_3NH is more likely to be produced in interstellar space. We have performed calculations for this species using methods identical to those used by Wilson (1978) for the isocyano isomer. The C_3N skeleton was assumed to be linear, but the possibility of an off-axis hydrogen was considered, with the result that the molecule is predicted to be linear. C_3NH is predicted to be less stable than the metastable HC_2NC , lying about 50 kcal per mol above the stable HC_3N form. The rotation constant is predicted to be 4.65 GHz with an estimated uncertainty of 1%. Information on HC_2NC and C_3NH is summarized in Table 3. The hyperfine structure due to the nitrogen nuclear quadrupole moment has not been computed for either of these metastable species, but is expected to be small by analogy with HNC ; it is probably unresolvable in interstellar sources.

f) Methyl Cyanide (H_3CCN)

Methyl cyanide (acetonitrile) is a well-known interstellar molecule. Its synthesis in space is uncertain; one possible path, tentatively explored by Smith and Adams (1978), is via a radiative association reaction sufficiently rapid to occur on every collision:



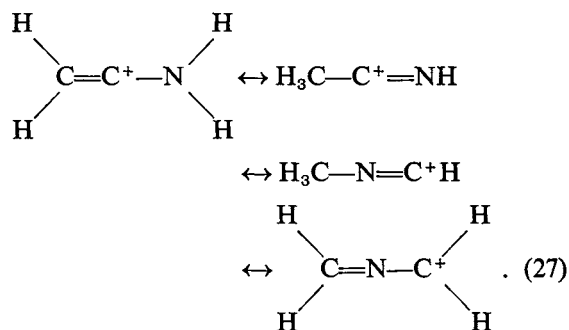
and/or



another speculative possibility is via



We estimate that equations (24)–(25) followed by dissociative recombination can produce a CH_3CN fractional abundance of $\sim 10^{-10}$. The structure of the protonated species in equations (24)–(26) is not known, but, based on standard valence bond structures, several likely (meta-)stable forms should exist, e.g.,

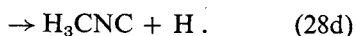
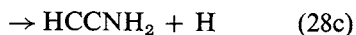
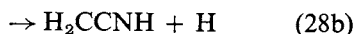


By analogy with other chemical species, it is likely that structures with a cyano (CCN) skeleton are more stable than those with the isocyano (CNC) skeleton.

TABLE 3
HCCNC AND CCCNH

Parameter	Value and Accuracy	Reference
Rotation constant (GHz):		
HCCNC.....	5.08 (1%)	Wilson (1978)
CCCNH.....	4.65 (1%)	This work
Excitation energy (kcal per mol):		
HCCNC.....	19 (20%)	Wilson (1978)
CCCNH.....	50 (20%)	This work

Depending on the structure(s) of the protonated precursor and on branching ratios in the dissociative recombination step, a variety of metastable species, as well as the observed methyl cyanide, can result from this primary synthesis:



Methyl isocyanide, H_3CNC (eq. [28d]), which lies about 17 kcal per mol above methyl cyanide (Liskow, Bender, and Schaefer 1972) has been well studied in the laboratory (Kessler *et al.* 1950). Based on analogy with HCN and HNC and on accurate laboratory frequencies, methyl isocyanide has been the subject of several radioastronomical searches, with negative results. The nondetection of methyl isocyanide might, at first glance, seem to argue against our thesis that metastable isomers are a rather general phenomenon in interstellar space. We suggest, however, that this is not the case, and that, in fact, the absence of methyl isocyanide is entirely consistent with the model presented here. If the ion-molecule reactions leading to the protonated precursor $\text{C}_2\text{H}_4\text{N}^+$ result in a "thermal" product distribution, as expected, the more stable "CCN" species will be formed in reactions (24)–(26). This preference will be even more likely in a secondary synthesis where $\text{C}_2\text{H}_4\text{N}^+$ is formed principally from protonation of H_3CCN . Then our model predicts that only ketenimine (H_2CCNH ; eq. [28b]) and ethynyl amine (HCCNH_2 ; eq. [28c]) are likely interstellar species. These have been predicted (Radom, Hehre, and Pople 1971) to lie 45 and 42 kcal per mol, respectively, above methyl cyanide. Both will have the spectra of slightly asymmetric tops. Although an accurate calculation of their spectral constants has not yet been done, an estimate could be made based on standard molecular geometries.

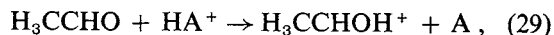
g) Acetaldehyde (H_3CCHO)

Acetaldehyde has been observed in an interstellar source (Gilmore *et al.* 1976, and references therein). Although it appears to have modest abundance, an accurate estimate is difficult since the excitation mechanism is uncertain; it has been suggested by

Fourikis *et al.* (1974) that it may be showing weak maser amplification. The interstellar synthesis of this species is poorly understood.

Isomerism between aldo and enol forms of aldehydes is a well studied phenomenon in organic chemistry. Theoretical calculations (Radom, Hehre, and Pople 1971; Bouma, Poppinger, and Radom 1977) predict ethenol (vinyl alcohol, H_2CCHOH) to lie only 10–15 kcal per mol above the stable acetaldehyde form and to have a large barrier (about 80 kcal per mol) against unimolecular rearrangement. Until a few years ago it was generally thought that ethenol, the simplest enol, was so short-lived that it could not be isolated or studied under laboratory conditions. However, Saito (1976) was able to synthesize it *in situ* and measure its microwave spectrum; his results are included in Table 4.

The possibility that ethenol exists in interstellar space has not escaped notice, and, based on known laboratory frequencies, several transitions have been looked for (Guélin 1978). Results to date have been negative, with sensitivity limits about a factor of two below the observed acetaldehyde intensities. If acetaldehyde and ethenol are both produced via a common ion precursor, and if the branching ratio in the dissociative recombination step is near unity, then we would expect a sufficient abundance of interstellar ethenol to have been detected. If ethenol is not formed via such a primary synthesis, it may still be produced via a secondary sequence because acetaldehyde can be protonated by species such as H_3^+ ,



If only this latter synthetic route is possible, however, we predict that ethenol is produced in quantities at or below the limit of detection with present sensitivity.

h) Ketene (H_2CCO)

The apparent paucity of carbon–carbon double bonds among interstellar molecules has proved quite puzzling. Ketene, one of the simplest such molecules, is quite similar to known interstellar species such as H_2CO , H_3CCHO , and $\text{H}_3\text{CCH}_2\text{OH}$, and had long been sought by radioastronomers. It has recently been detected in a dense cloud (Turner 1977), although its

TABLE 4
ETHENOL (H_2CCHOH), VINYL ALCOHOL

Parameter	Value and Accuracy	Reference
Rotation constants (GHz):		
A.....	59.6602 \pm 0.0023	Saito 1976*
B.....	10.56155 \pm 0.00048	Saito 1976
C.....	8.96582 \pm 0.00042	Saito 1976
Dipole moment (D)	1.016 \pm 0.009	Saito 1976
Excitation energy (kcal per mol)....	12 \pm 2	Bouma <i>et al.</i> 1977

* Some of the reported measured frequencies deviate by tens of MHz from the rigid rotor values obtained from these constants.

TABLE 5
ETHYNOL (HCCOH)

Parameter	Value and Accuracy	Reference
Rotation constants (GHz):		
<i>A</i>	666.0 (10%)	Dykstra 1978
<i>B</i>	9.73 (1%)	Dykstra 1978
<i>C</i>	9.59 (1%)	Dykstra 1978
Excitation energy (kcal per mol).....	35 (10%)	Dykstra 1978

abundance is rather low. The interstellar chemistry of ketene seems poorly understood.

Ketene has several metastable isomeric forms which have been the subject of theoretical investigations (Strausz, Gosavi, and Gunning 1978; Dykstra 1978) since they are prototypical of species thought to play important roles in organic rearrangement reactions. The lowest lying of these, predicted to be about 30 kcal per mol above ketene, is ethynol (HCCOH). The possibility that this species exists in interstellar clouds (with perhaps greater abundance than ketene) is intriguing, but is suggested by the fact that the acetylenic triple bond seems to be particularly favored in the interstellar environment, with several substituted acetylenes observed, and by the fact that both methyl and ethyl alcohol are observed.

Ethynol is a slightly asymmetric top, being linear except for the off-axis hydroxyl hydrogen atom. Its predicted rotational constants are in Table 5.

It should be mentioned that other, less stable isomers of ketene have also been studied. Two of these, which have a cyclic COC skeleton, are oxirene and oxiranylidene. These are predicted to lie between 70 and 90 kcal per mol above ketene.

IV. CONCLUSIONS

In this paper we have considered the possibility that organic reactive intermediates exist in dense interstellar clouds in sufficient abundances for observation by radioastronomical techniques. The particular class of compounds considered—metastable isomers of selected neutral species—can be formed with non-thermal distributions in dissociative recombinations of positive ions with electrons. Current ideas of gas-phase interstellar chemistry suggest that some of these metastables may be quite abundant. As radio observations continue to improve, we expect that many such molecules, of transient existence in the laboratory, will be discovered in space, thus greatly enhancing our knowledge of both interstellar and terrestrial chemistry. In this context, it is noteworthy that several dozen interstellar microwave spectral lines, some of them relatively strong, remain unidentified. We hope that an increased awareness of the importance of these metastable species will prompt more refined quantum chemical calculations, further laboratory effort, more radioastronomical searches, and generally a more persistent effort at identifying the as-yet-unidentified interstellar signals.

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APPENDIX

We consider here the concentration ratio of a metastable isomer, A^* , to its lowest energy form, A , which may be attained solely via a secondary synthesis. Thus, it is assumed that the dominant formation mechanism of A does *not* involve a precursor protonated ion whose dissociative recombination with an electron yields A and possibly also A^* ; we have referred to such a reactive sequence as a primary synthesis.

We make the following assumptions: (1) Species A^* is depleted only by reaction with ions. The important question here is whether metastable species, unlike most stable species, can be destroyed rapidly by reacting with neutrals. Since the breaking of bonds in neutral-neutral reactions generally has an activation barrier, these normally proceed very slowly at interstellar temperatures. As long as a metastable species has a closed-shell electronic structure, it should also have activation barriers against reaction with neutrals. However, some of the metastables have open-shell (triplet) electronic structures, and these *may* react rapidly, without activation barriers, with neutral atoms and radicals; in that case the metastable could have significantly lower abundance than predicted in this model. (2) The protonated precursor ion, AH^+ , is depleted mainly (or at least competitively) via dissociative recombination with electrons. Thus, the relevant protonated species must not react rapidly with H_2 . Reaction with O , O_2 , and other abundant heavy neutrals can reduce our estimated metastable abundances somewhat. (3) All ion-molecule reactions, if they proceed at all, occur at the Langevin rate k_L . Also, we assume that all electron dissociative recombinations occur at a rate k_e .

Consider the following sequence of reactions which constitute a secondary synthesis:



We have used the following notation: I^+ represents all interstellar positive ions (n.b. $[I^+] = [e]$, the electron concentration); AH^+ is the ion formed by protonating A or A^* (n.b. we avoid here questions concerning possibly different, metastable structures of this ion); f and f^* are the fractions of the total ion abundance $[I^+]$ able to protonate species A and A^* , respectively; f' is the fraction of the total ion abundance $[I^+]$ which reacts with A^* , but does not protonate it; g and g^* are the fractions of dissociative recombinations of AH^+ leading to A and A^* , respectively.

If we then make the steady-state assumption, it can be shown that the ratio of concentrations of A^* to A is given by

$$\frac{[A^*]}{[A]} = \frac{g^*f}{f^*(1 - g^*) + f'} \quad (\text{A4})$$

The denominator on the right-hand side of equation (A4) is less than or equal to unity. It approaches unity when, for example, $f' \approx 1$ and $f' \gg f^*$. This situation occurs when most of the interstellar ions react with A^* but do not protonate it. (Such a situation would occur if C^+ were the dominant ion.) Under these circumstances, the $[A^*]$ to $[A]$ ratio reaches a lower limit of g^*f , where $f \approx f^*$ is considerably less than unity. If, however, f , f^* , and f' are the same order of magnitude, or if $f \approx f^* > f'$, then the $[A^*]$ to $[A]$ ratio can approach unity. Both limits must be considered within the realm of possibility, given the uncertainties in models of dense cloud chemistry.

Note added in proof.—After the completion of this work we learned of a new, large-scale quantum calculation on HCCOH by M. Yoshimine, IBM Research Laboratory. This work, unlike previous studies, did not constrain the HCCO group to be linear, with the result that a slightly bent configuration is predicted. Rotation constants (in GHz) from this calculation are $A = 665$, $B = 9.67$, and $C = 9.54$; these fall within the uncertainty in the values given in Table 5 but are thought to be somewhat more accurate. We thank Dr. Yoshimine for providing his results prior to publication.

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